Synthesis and Polymerization of an Optically Active Bifunctional Disiloxane. 2. Preparation of Optically Active (*S*)-2-(1-Naphthyl)-2-phenyl-5,5-dimethyl-1-oxa-2,5-disilacyclopentane and Its Ring-Opening Polymerization

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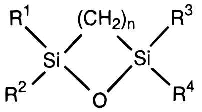
ABSTRACT: An optically active (>98.2% ee) five-membered cyclic silicon compound, (*S*)-2-(1-naphthyl)-2-phenyl-5,5-dimethyl-1-oxa-2,5-disilacyclopentane, was synthesized by intramolecular hydrosilylation of (1*S*)-1-(1-naphthyl)-1-phenyl-1-vinyl-3,3-dimethyl-3-hydro-1,3-disiloxane in good yield (as high as 74.3%). This cyclic compound could be easily polymerized by common nucleophilic initiators, such as PhLi, MeONa, and *t*-BuOK. The polymerization using the lithium initiator showed a very high regioselectivity in ring opening (head-to-tail content 98.7% at 0 °C) and consequently afforded an optically active and highly isotactic poly[{(1*S*)-1-(1-naphthyl)-1-phenyl-3,3-dimethyldisiloxane-1,3-diyl}ethylene] ($[\alpha]^{25}_{D} = -8.5°$, $M_n = 20\,800$ (calculated from ^{29}Si NMR), $M_w/M_n = 1.12$ (by SEC)).

Introduction

The increasing interest in recent years in silicon-containing polymers applicable as electronic and optical materials, ceramics precursors, etc.,[1] has promoted the development of silicon-containing polymers with a well-controlled molecular weight and molecular weight distribution, as well as a well-controlled microstructure.[2,3] The ring-opening polymerization (ROP) of cyclic silicon compounds[4] is the most promising method to achieve the above goals, as is the only practical chain polymerization method available for silicon compounds because of the nonexistence of stable multiple bonds involving silicon atoms.[5] To date, intense efforts have been focused on the use of ROP for preparing poly(siloxane)s,[6] poly(silane)s,[2] and poly(carbosilane)s.[3] On the other hand, little attention has been paid to the synthesis of poly(carbosiloxane)s from cyclic carbodisiloxanes,[7−9] a group of cyclic compounds represented by the general structure **I** (Figure 1).[7,10] In as early as 1960, Piccoli first reported the anionic ROP of methyl- and/or phenyl-substituted five-membered rings of this type and obtained high molecular weight polymers.[7] Lately, more detailed research on the polymerization of these compounds has shown that this is a very efficient way to prepare poly(carbosiloxane)s of high molecular weight (M_n = ∼130 000) and relatively narrow molecular weight distribution ($M_w/M_n = 1.28−1.66$).[8,9]

In our previous work,[11] the synthesis of an optically active poly(carbosiloxane), poly[{(1*S*)-1-(1-naphthyl)-1-phenyl-3,3-dimethyldisiloxan-1,3-diyl}ethylene] ((*S*)-**3**), via hydrosilylation was reported (Scheme 1). However, this method suffered some drawbacks, such as the rather low yield (37.8%) and low molecular weight (M_n = 2900, polystyrene standard) of the polymer obtained. Along with the polymer, in the hydrosilylation a considerable amount of the cyclic compound (*S*)-2-(1-naphthyl)-2-phenyl-5,5-dimethyl-1-oxa-2,5-disilacyclopentane ((*S*)-**1**) (26.3%) was also formed.

In this paper, we report the reaction conditions for the high yield formation of (*S*)-**1** and the results of our investigation of the anionic ROP of this cyclic compound.



I

Figure 1. The general structure of cyclic carbodisiloxanes.

Polymerization of (*S*)-**1** using phenyllithium (PhLi) as an initiator was highly regioselective and afforded a high molecular weight poly[{(1*S*)-1-(1-naphthyl)-1-phenyl-3,3-dimethyldisiloxane-1,3-diyl}ethylene], with a narrow molecular weight distribution, in high yield.

Experimental Section

Analytical Methods. The analytical methods employed are similar to those in the former report.[11]

(*S*)-2-(1-Naphthyl)-2-phenyl-5,5-dimethyl-1-oxa-2,5-disilacyclopentane ((*S*)-1) (Scheme 1). In a 300 mL flask were added 94.0 g of xylene and the platinum−1,3-divinyl-1,1,3,3-tetramethyl-1,3-disiloxane complex (Pt−DVTMDS)[12] (2.3×10^{-2} mmol of Pt, 2.3 mL of 0.01 M benzene solution) and heated to 80 °C. Then a (1*S*)-1-(1-naphthyl)-1-phenyl-1-vinyl-3,3-dimethyl-3-hydro-1,3-disiloxane[11] ((*S*)-NPVDMDS) solution (15.7 g, 0.0468 mol, in 47.0 g of xylene) was added dropwise for 18 h. After another 18 h, the reaction was completed according to the IR analysis. The SEC analysis of the product mixture showed that the yield of (*S*)-**1** was 74.3%. Distillation of the product mixture gave a white waxy solid (*S*)-**1** (8.3 g, 52.9%). The direct mixing of (*S*)-NPVDMDS, catalyst, and solvent from the initial stage gave a lower yield (53.1% estimated by SEC). Calculated molecular weight: 334.57.

MS: *m*/*e* 335 (M + 1), 319 (M − Me), 257 (M − Ph), 207 (M − Np). ^{1}H NMR: δ 0.24 and 0.344 (two s, 3 H, each SiCH_3), 0.89−1.05 (m, 2 H, $CH_2CH_2Si(CH_3)_2$), 1.44−1.54 (m, 2 H, $CH_2CH_2Si(CH_3)_2$), 7.29−8.02 (m, 12 H, Np and Ph). ^{13}C NMR: δ 0.26 and 0.38 (two SiCH_3), 8.49 ($CH_2CH_2Si(CH_3)_2$), 9.32 ($CH_2CH_2Si(CH_3)_2$), 125.24, 125.62, 125.98, 127.98, 128.70, 128.82, 129.95, 130.6, 133.32, 134.15, 134.45, 136.91, 137.03 (Np and Ph carbons). ^{29}Si NMR: δ 4.97 (m, *Si*(NpPh)), 27.10 (m, *Si*(CH_3)$_2$). IR (neat): 3068−2895, 1252, 914 (υ_{SiOSi}) cm^{-1}. $[\alpha]^{25}_{D} = -17.5°$ (*c* 1.18, 1,4-dioxane). Bp: 121−5 °C/0.09 mmHg. Mp: 74−76 °C.

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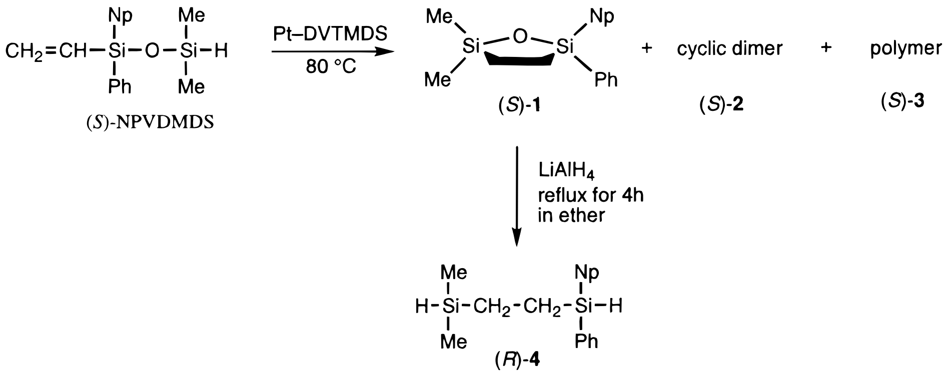
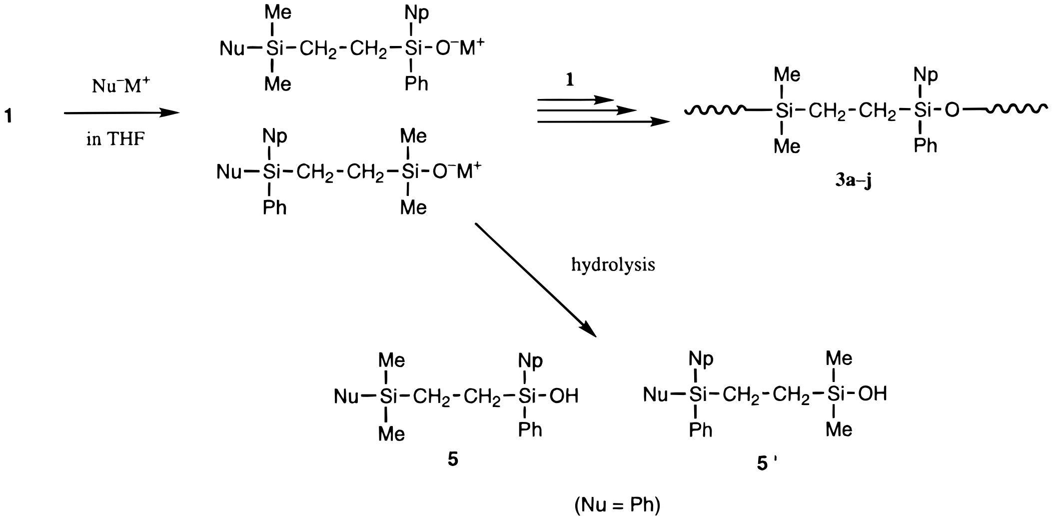
Scheme 1



Scheme 2



Racemic 2-(1-naphthyl)-2-phenyl-5,5-dimethyl-1-oxa-2,5-disilacyclopentane ((*rac*)-**1**), a viscous liquid, was prepared similarly.

(*R*)-1-(1-Naphthyl)phenylsilyl-2-dimethylsilylethane ((*R*)-4) (Scheme 1). To a (*S*)-**1** solution (0.79 g, 2.3 mmol, in 5 mL of diethyl ether) in a 30 mL flask was added 1 M $LiAlH_4$ in diethyl ether solution (4.6 mL, 4.6 mmol) and heated to reflux for 4 h. After evaporating the ether, *n*-hexane was added, and the mixture was filtered under anhydrous conditions. Removing the solvent gave (*R*)-**4** (0.70 g, 94.9%). Calculated molecular weight: 320.59. MS: *m*/*e* 319 (M − 1), 305 (M − Me), 243 (M − Ph), 193 (M − Np). ^{1}H NMR: δ 0.07 (d, 6 H, $Si(CH_3)_2H$, J = 3.7 Hz), 0.67−0.71 (m, 2 H), 1.24−1.29 (m, 2 H), 3.85 (m, 1 H, $Si(CH_3)_2H$), 5.24 (t, 1 H, Si(NpPh)*H*, J = 3.9 Hz), 7.32−8.06 (m, 12 H, Np and Ph). IR (neat): ν 3068−2895, 2113 (υ_{SiH}), 1506, 1428, 1249 cm^{-1}.

Racemic 1-(1-naphthyl)phenylsilyl-2-dimethylsilylethane (*rac*)-**4** was prepared in the same way.

1-Hydroxy(1-naphthyl)phenylsilyl-2-dimethylphenylsilylethane (5) (Scheme 2). Phenyllithium (PhLi) (3.17 mmol, 3.37 mL of 0.94 M solution in cyclohexane−diethyl ether) was added to a 30 mL flask and cooled to 0 °C. Then a (*S*)-**1** solution (0.53 g, 1.58 mmol, in 3.5 mL of THF) was added dropwise in 15 min. After reacting for 2 h, the product mixture was poured into 100 mL of phosphate buffer solution (pH = 7), extracted with diethyl ether, and washed with water for three times, followed by drying over $MgSO_4$. Evaporating the solvent gave a viscous colorless liquid comprising of almost **5** (0.66 g, ~100%). Small amounts of 1-(1-naphthyl)diphenyl-2-hydroxydimethylethane (**5′**) and some oligomers were also formed which were not removed for the structure analysis. ^{1}H NMR: δ 0.25 and 0.26 (two s, 3 H, each $SiCH_3$), 0.80−0.84 (m, 2 H), 1.21−1.25 (m, 2 H), 2.30 (s, 1 H, Si(NpPh)O*H*), 7.30−8.09 (m, 17 H, Np and Ph). ^{13}C NMR: δ − 3.78 and − 3.74 (two $SiCH_3$), 7.01 and 8.01 ($Si(NpPh)CH_2CH_2Si(Me_2)$), 125.05−139.00 (Np and Ph). ^{29}Si NMR: δ −1.61 (*Si*(NpPh)OH), −0.89 ($Si(CH_3)_2Ph$). IR (neat): ν 3367 (υ_{SiOH}), 3068−2792, 1506, 1427, 1249, 1113 cm^{-1}.

Synthesis of Poly[{1-(1-naphthyl)-1-phenyl-3,3-dimethyldisiloxane-1,3-diyl}ethylene] (3a−j) (Scheme 2). The procedure for synthesizing **3a** is given as a typical example. In a 5 mL flask under anhydrous argon atmosphere were added (*S*)-**1** (1.02 g, 3.05 mmol) and anhydrous THF (2.29 mL, 2.04 g) and cooled to 0 °C, and then PhLi (0.051 mmol, 54.3 μL of 0.94 M solution in cyclohexane−diethyl ether) was added. After reacting for 67 h, a small amount of dilute HCl solution was added to stop the reaction. Reprecipitation from $CHCl_3$ into methanol afforded a white polymeric material **3a** (yield 93%). SEC: M_n = 11 300, M_w/M_n = 1.12. ^{1}H NMR: −0.33 to 0.05 (m, 6 H, $SiCH_3$), 0.30−0.50 (br, 2 H, $CH_2CH_2Si(CH_3)_2$), 0.85−1.18 (br, 2 H, $CH_2CH_2Si(CH_3)_2$), 6.93−8.14 (br, 12 H, Np and Ph). ^{13}C NMR: δ −0.56 and −0.43 ($Si(CH_3)_2$), 7.72 ($CH_2CH_2Si(CH_3)_2$), 9.52 ($CH_2CH_2Si(CH_3)_2$), 124.93, 125.37, 125.57, 127.72, 128.70, 128.79, 129.36, 130.35, 133.34, 134.09, 134.64, 134.71, 135.25, 136.92, and 137.80 (Np and Ph). ^{29}Si NMR: δ −10.7, 10.4. IR (neat): ν 3068−2874, 1254, 1066 (υ_{SiOSi}) cm^{-1}. $[\alpha]^{25}_{D} = -8.5°$ (c 1.21, 1,4-dioxane).

3b−j were prepared similarly to **3a** (refer to Table 1).

Results and Discussion

Synthesis and Characterization of (*S*)-1. *Synthesis.* Hydrosilylation of (1*S*)-1-(1-naphthyl)-1-phenyl-1-vinyl-3,3-dimethyl-3-hydro-1,3-disiloxane ((*S*)-NPVDMDS) under neat bulk conditions gave mainly three products: the cyclic monomer (*S*)-**1**, the cyclic dimer (*S*)-**2**, and the polymer (*S*)-**3** (Scheme 1), in the yields of 26.3%, 35.9%, and 37.8%, respectively.[11] To obtain a higher yield of cyclic products, reaction conditions preferable for intramolecular reaction must be chosen.

Table 1. Anionic Ring-Opening Polymerization of (*S*)-1 and (*rac*)-1 in THF Solution[a]

				M_n				
polymer	monomer	time	yield, %	by SEC (M_w/M_n)[b]	by ^{29}Si NMR[c]	from yield[d]	H−T, %[e]	$[\alpha]^{25}{}_D$[f]
3a	(*S*)	67 h	93	11300 (1.12)	20800	18700	98.7	−8.0 (*c* 1.62)
3b		24 h	87	5900 (1.15)	7800	8700	98.7	−8.5 (*c* 1.61)
3c		15 h	92	6800 (1.14)	8800	9200	97.6	−8.3 (*c* 1.56)
3d	(*rac*)		92	4400 (1.19)	6200	9200	98.0	
3e	20% (*S*) + 80% (*rac*)		93	6000 (1.19)				−1.3 (*c* 1.67)
3f	40% (*S*) + 60% (*rac*)		96	4700 (1.20)				−2.9 (*c* 1.61)
3g	60% (*S*) + 40% (*rac*)		96	4500 (1.21)				−4.3 (*c* 1.58)
3h	80% (*S*) + 20% (*rac*)		96	4600 (1.20)				−5.8 (*c* 1.55)
3i	(*rac*)		89	4700 (1.20)	3900	8900	89.4	
3j	(*S*)	10 min	81	10800 (2.60)	*g*	*g*	79.2	−6.6 (*c* 1.18)
		24 h	27	4400 (1.48)	*g*	*g*	61.4	−0.7 (*c* 1.14)

[a] $[M]_0$ = 0.92 mol/L; [I] = 0.015 (**3a**), 0.031 mol/L (**3b**−**j**); initiator: PhLi (**3a**−**h**), MeONa (**3i**), *t*-BuOK (**3j**); T = 0 °C (**3a**,**b**), 20 °C (**3c**−**j**). [b] Polystyrene standard. [c] Calculated from the integral ratio of overall *Si*(NpPh) and chain end *Si*(NpPh)OH in ^{29}Si NMR spectra. [d] Calculated from polymer yields and monomer/initiator ratios. [e] H−T, % = H−T/(H−T + H−H + T−T) = $A/(A + B) \times 100$, where A and B are the integral area of β- and β'-silicon atoms estimated by ^{29}Si NMR, respectively (see Figures 4 and 5). [f] In 1,4-dioxane. [g] Inapplicable for containing cyclic structures.

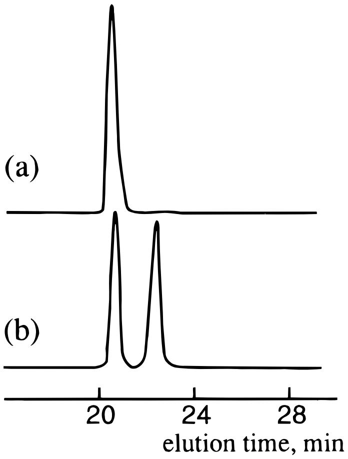


Figure 2. HPLC chromatograms performed on an optically active stationary phase (flow rate 0.6 mL/min, column temperature 35 °C, eluent *n*-hexane[11]): (a) (*R*)-**4** and (b) (*rac*)-**4**.

Since the dilution of the reaction system should favor the intramolecular reaction, xylene was used as a solvent (xylene/(*S*)-NPVDMDS = 9/1 (wt)). In the case of initial mixing of (*S*)-NPVDMDS, catalyst, and the solvent, the yield of (*S*)-**1** increased steadily from 35.4% to 53.1% as the reaction temperature increased from 30 to 80 °C. Temperatures higher than 80 °C, however, did not further enhance the yield of (*S*)-**1**. To keep the concentration of (*S*)-NPVDMDS in the reaction system at a low level, a solution of (*S*)-NPVDMDS (xylene/(*S*)-NPVDMDS = 3/1 (wt)) was added slowly to a flask containing the catalyst solution (2.1×10^{-5} M Pt−DVTMDS in xylene) for 18 h and then reacted for another 18 h. In this manner, as high as 74.3% yield of (*S*)-**1** was obtained.

*Characterization and Determination of the Optical Purity of (S)-**1**.* The assignment of (*S*)-**1** was made mainly on the basis of the ^{1}H−^{1}H and ^{1}H−^{13}C COSY, NOE, and DEPT NMR results. The chemical shifts in the ^{29}Si NMR spectrum are appreciably higher (5.0 and 27.1 ppm) than those of the corresponding polymer (*S*)-**3** (−10.7 and 10.4 ppm),[11] reflecting the highly strained structure of this cyclic compound. This effect is also observed in the IR spectrum, which showed a much lower ≡SiOSi≡ stretching band at 914 cm^{-1} than that of the polymer (*S*)-**3** (1066 cm^{-1}).

The optical purity of (*S*)-**1** was determined by analyzing the optical purity of its reduced product (*R*)-**4** (Scheme 1). Figure 2 presents the results of the HPLC analysis on an optically active stationary phase, indicating that (*R*)-**4** is 98.2% ee, and consequently the optical purity of (*S*)-**1** is 98.2% ee or higher.

Anionic Ring-Opening Polymerization of (*S*)-1. *Polymerization*. According to Suryanarayana,[8] the infrared absorption frequency of the ≡SiOSi≡ unit correlates to the strain energy. In the case of the methyl- and/or phenyl-substituted five-membered cyclic carbodisiloxanes, the IR absorption of the ≡SiOSi≡ unit ranged from 910 to 924 cm^{-1}, and the strain energy was estimated to be 8−12 kcal/mol.[7] As mentioned above, the cyclic monomer (*S*)-**1** shows an IR absorption of the ≡SiOSi≡ unit at 914 cm^{-1} and hence is supposed to have a similar strain energy. Polymerization of (*S*)-**1** was carried out in THF using PhLi, sodium methoxide (MeONa), and potassium *tert*-butoxide (*t*-BuOK) as initiators (Scheme 2 and Table 1). PhLi and MeONa afforded rather high yields (87−96%) of polymers with narrow molecular weight distributions (M_w/M_n = 1.12−1.21) (**3a**−**i**). On the other hand, polymerization utilizing *t*-BuOK (**3j**) showed very different characteristics. At the early stage (after 10 min) of the polymerization, the yield and the molecular weight of polymer formed were high (yield 81%, M_n = 10 800 (by SEC)), but after reacting for 24 h, both the yield and the molecular weight of the obtained polymer decreased significantly (yield 27%, M_n = 4400 (by SEC)). The SEC trace of the products of **3j** during the polymerization clearly revealed this tendency (Figure 3). This result and the following ^{29}Si NMR analysis indicated that a chain scission reaction occurred on the polymer chains both intramolecularly (backbiting) and intermolecularly, very similar to the case of the anionic polymerization of ϵ-caprolactone using *t*-BuOK as an initiator.[13] That is, at the early stages of the polymerization, the chain propagation and the chain scission proceeded simultaneously, and the propagation is faster than the chain scission. When most of the monomer is consumed, the chain scission became predominant, and the high molecular weight linear polymer chains were cleaved into lower molecular weight cyclic polymers (the structures of these polymers were proven by ^{29}Si NMR and IR analysis and will be discussed in the next section) and stable cyclic oligomers. The major components of the cyclic oligomers were supposed to be the cyclic dimer according to the MS (*m*/*e*: 669 (M + 1), 591 (M − Ph), 541 (M − Np)), SEC (M_w/M_n = 1.04), and IR analyses, although their NMR spectra are too complicated to allow a determination of their stereochemical structures.

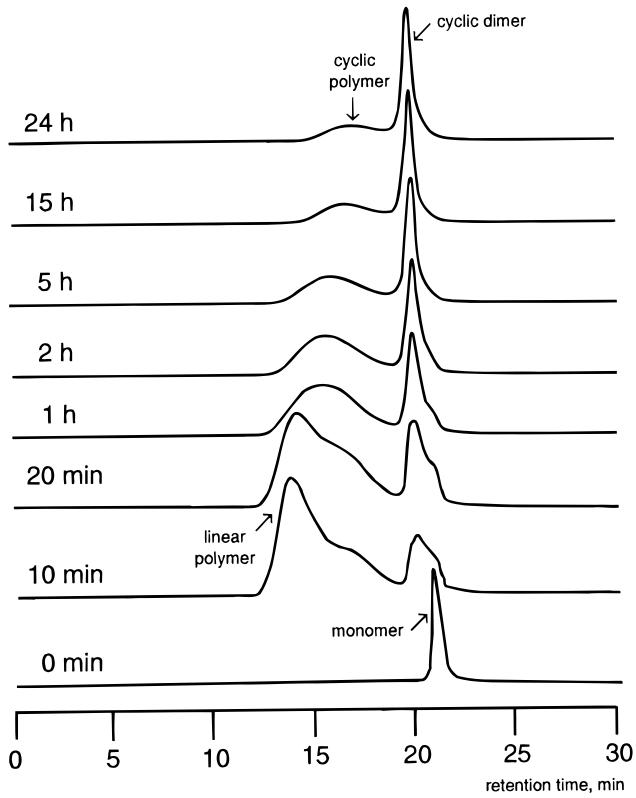


Figure 3. SEC trace of polymerization products of **3j**.

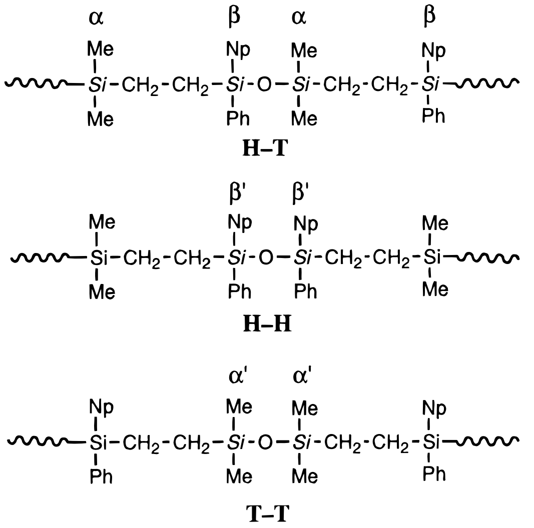


Figure 4. Possible sequence structures of polymer **3**.

Regioselectivity and Mechanism of Polymerization. The attack of a nucleophile could possibly occur on the *Si*(Me)$_2$ or *Si*(NpPh) of (*S*)-**1**, which would thus result in the production of **5** and **5′** in the initiation step (Scheme 2) and the possible formation of three kinds of disiloxane linkage, i.e., the head-to-tail (H−T), head-to-head (H−H), and tail-to-tail (T−T) structures in the propagation step (shown in Figure 4). To clarify the initiation step of the polymerization, (*S*)-**1** was reacted with excess PhLi, and an initial product mixture of **5** and **5′** was obtained. The two major peaks at −1.2 and −0.9 ppm in Figure 5a are assigned to be the *Si*(NpPh)-OH and *Si*Me$_2$Ph of **5**, respectively, referring to the chemical shift of the model compound **7** (Table 2) and to the fact that when the initiator was changed to MeONa, the peak at lower field disappeared, while the peak at higher field remained (refer to Figure 5c). A very small peak at 18.5 ppm in Figure 5a is considered to be the *Si*(Me)$_2$OH of **5′**, judging from the chemical shifts of the model compounds **6**, **10**, and **11** in Table 2. The integral ratio of *Si*(NpPh)OH and *Si*(Me)$_2$OH is about 92/8. Therefore, it can be concluded that the initiation step of the polymerization using PhLi as an initiator is highly regioselective; i.e., PhLi predominantly attacked the silicon atom of *Si*(Me)$_2$ rather than the *Si*(NpPh).

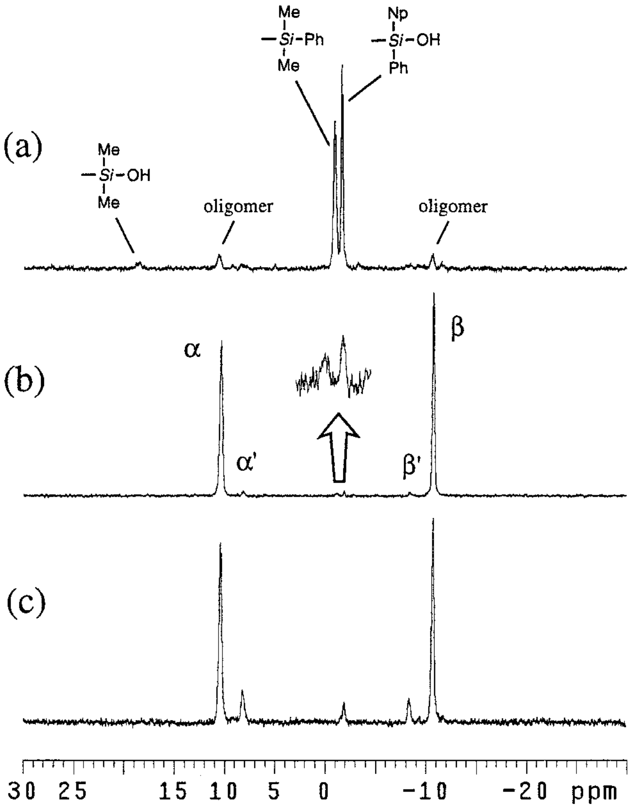


Figure 5. ^{29}Si NMR spectra of (a) the mixture of **5** and **5′**, (b) **3a**, and (c) **3i**.

Table 2. ^{29}Si NMR Chemical Shifts of Some Silicon Compounds

compound	chemical shift, ppm
Me_3SiOH (**6**)	16.5
MeNpPhSiOH (**7**)[14]	−0.9
$Me_3SiOSiMe_3$ (**8**)	7.3
MeNpPhSiOSiPhNpMe (**9**)[14]	−8.4
$HO\{Si(Me)_2(CH_2)_6Si(Me)_2O\}_nH$ (**10**)[15a]	SiOH, 18.0; SiOSi, 7.3
$HO\{Si(Me)_2C_2H_4C_6F_{12}C_2H_4Si(Me)_2O\}_nH$ (**11**)[15b]	SiOH, 17.5; SiOSi, 8.4

In the ^{29}Si NMR spectrum of polymer **3a** prepared by using PhLi (Figure 5b), the major signals at −10.7 and 10.4 ppm can be undoubtedly assigned to the H−T structure by reference to the known structure of (*S*)-**3**. Clarification of the minor peaks at −8.4, −1.9, −1.2, and 8.1 ppm is also important because these peaks may reveal the structural sequence of this polymer and the mechanism of polymerization. The two peaks at −1.9 and −1.2 ppm of polymer **3a** clearly correspond to the peaks at −1.2 and −0.9 ppm of the initial product **5** (Figure 5a) and are therefore assigned to be the chain end *Si*(NpPh)OH and the initial terminal *Si*Me$_2$Ph, respectively. Because there is no visible chain end, *Si*(Me)$_2$OH, in polymer **3a** (Figure 5b), the propagation

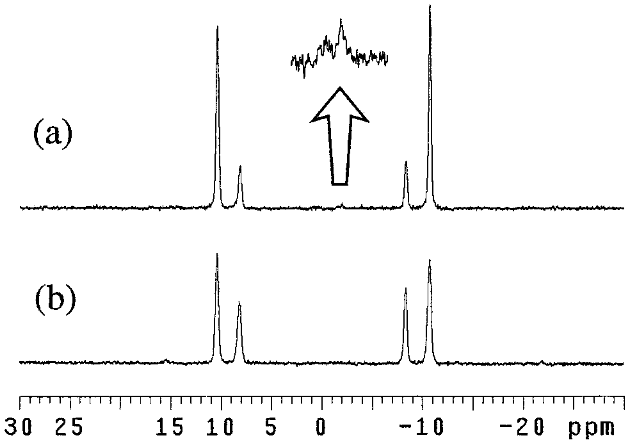


Figure 6. ^{29}Si NMR spectra of **3j** (a) after 10 min and (b) after 24 h.

step of the polymerization seems to proceed highly regioselectively to give the *Si*(NpPh)OH chain end.

Based on the model compounds **8**−**11** (in Table 2), the peaks at −8.4 and 8.1 ppm of **3a** were ascribed to the H−H and T−T structure, respectively. Consequently, the H−T content of **3a** is calculated to be 98.7%. The results of polymerization under other reaction conditions are calculated in the same way and also summarized in Table 1. Apparently, the countercation of the initiator influences the H−T content of the polymer formed greatly, following the order Li^+ (**3c**, 97.6%) > Na^+ (**3i**, 89.4%) > K^+ (**3j**, 79.2% (at 10 min)), and a lower polymerization temperature leads to a higher H−T content, e.g., in the case of Li^+, 0 °C, 98.7% (**3a**) > 20 °C, 97.6% (**3c**).

The calculated M_n of **3a** based on the ^{29}Si NMR spectrum is about 20 800, which is quite consistent with the value calculated from the monomer/initiator ratio and the polymer yield (M_n = 18 700), and the results obtained for other polymers prepared by using PhLi, **3b**−**d**, also showed good agreement (Table 1). This is evidence for the linear structure of these polymers and also indicates that the M_n estimated by SEC using a polystyrene standard (Table 1) is lower than the real value. In the case of **3i** prepared by using MeONa, however, the M_n calculated by ^{29}Si NMR (3900) is much lower than the calculated value from the polymer yield (8900) and even lower than the SEC result (4700). This might be explained by considering that the amount of the *Si*(NpPh)OH may be overestimated since the signal of the initial terminal of this polymer may appear at the same position as that of the chain end *Si*(NpPh)OH.

Polymer **3j** prepared by using *t*-BuOK is quite different from the polymers prepared by using PhLi or MeONa. Ten minutes after the start of the polymerization (Figure 6a), the polymer formed exhibited a small signal due to *Si*(NpPh)OH at −1.9 ppm, which reflected the linear part of this polymer; after 24 h (Figure 6b), however, the peak of the chain end *Si*(NpPh)OH had disappeared (the IR spectrum (Figure 7) also showed almost no ≡SiOH absorption), suggesting the formation of cyclic structures. It is noticed that the H−T structure of polymer **3j** decreased from 79.2% to 61.4% (Table 1) as the polymerization time was increased from 10 min to 24 h. These facts indicate that the chain scission and the chain recombination caused by the rather active species $\equiv SiO^-K^+$ occurred in the later stages of the polymerization, which resulted in the redistribution of the polymer chains and thus a less ordered structure.

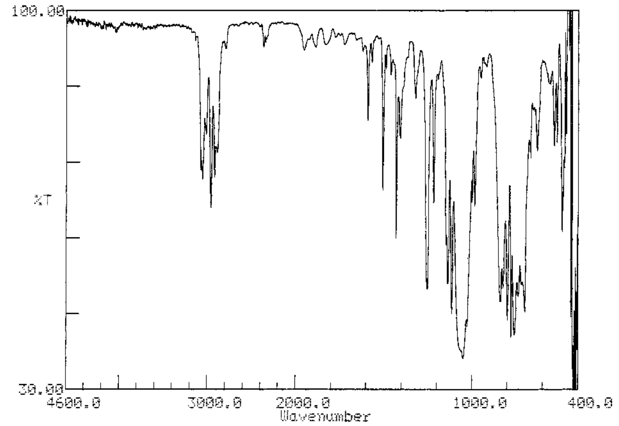


Figure 7. IR spectrum of **3j** (after 24 h).

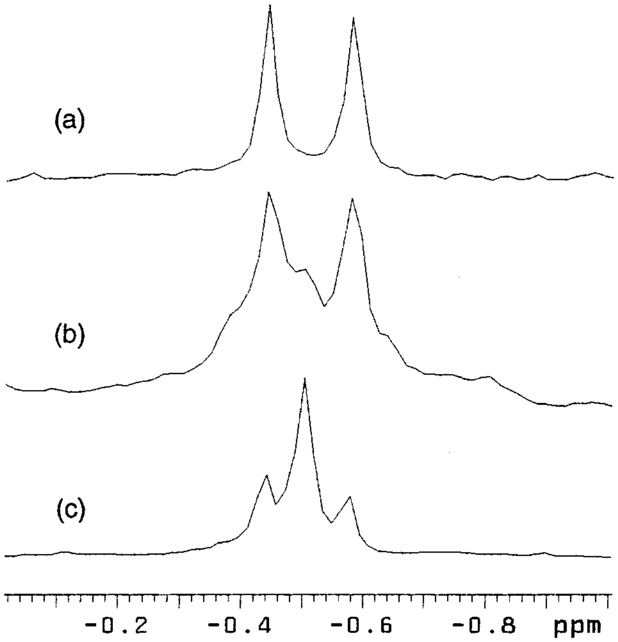


Figure 8. ^{13}C NMR spectra of the Si(CH_3)$_2$ region of (a) **3a**, (b) (*S*)-**3**, and (c) **3d**.

The Stereoregularity and Optical Activity of the Polymers. As discussed above, in the polymerization using PhLi as an initiator, the propagating anion $\equiv SiO^-$ attacked the achiral silicon atom *Si*(Me)$_2$ regioselectively, such that the absolute configuration of the asymmetric silicon atom of *Si*(NpPh) would be highly retained. Figure 8 shows the ^{13}C NMR spectrum of the Si(CH_3)$_2$ region of **3a**, along with those of (*S*)-**3** obtained by hydrosilylation and **3d** prepared from (*rac*)-**1**, for comparison. As reported in the previous paper,[11] the methyl groups on the Si(CH_3)$_2$ of (*S*)-**3**, functioning as a stereochemical probe, can provide information about the stereoregularity of this polymer. **3a** (Figure 8a) is similar to (*S*)-**3** (Figure 8b) but showed more clearly separated two peaks at −0.579 and −0.427 ppm, indicating its unambiguously high stereoregularity (isotacticity). On the other hand, **3d** (Figure 8c) showed three peaks at −0.579, −0.504, and −0.427 ppm, a typical atactic pattern, as expected.

The polymers **3a**−**c** showed an optical rotation which ranged from $[\alpha]^{25}_D$ = − 8.0 to −8.5° (in 1,4-dioxane);

these values, however, are not only different in magnitude but also opposite in sign to that of polymer (*S*)-**3** ($[\alpha]^{25}_{D} = +2.6°$ (*c* 1.88, in 1,4-dioxane)). The absolute configurations of the asymmetric silicon atoms in polymer **3a** and (*S*)-**3** should have the same (*S*)-form according to their polymerization mechanisms, and hence they should show optical rotations with the same sign. To investigate this phenomenon, a series of polymers **3f**−**i** were prepared from the combination of (*S*)-**1** and racemic (*rac*)-**1** (listed in Table 1). The optical rotations of these polymers are almost in direct proportion to the percentage of (*S*)-**1** incorporated. This polymerization showed no obvious preference for one of the two isomers of the monomer (the atactic polymer **3d** was obtained from the racemic monomer, Figure 8c), and the CD spectrum of **3a** showed no evidence of any preferred conformation. Thus, the different signs of the optical rotation of **3a** and (*S*)-**3** are not considered due to their different conformations. Since the molecular weight of (*S*)-**3** was quite low ($M_n = 2900$, estimated by SEC with a polystyrene standard), the effect of the terminal units in (*S*)-**3**, which possibly display a plus rotation, cannot be neglected and may result in the plus sign of the optical rotation of this polymer. Therefore, the optical rotation $[\alpha]^{25}_{D} = -8.5°$ (*c* 1.21, 1,4-dioxane) found for **3a**, with its rather high molecular weight ($M_n = 20\,800$, calculated from the ^{29}Si NMR spectrum) may approximate the genuine value of the internal repeating units of this isotactic polymer. It is noticed that, when *t*-BuOK was used as an initiator (**3j**), the polymer formed at the early stages (after 10 min) showed an optical rotation of $[\alpha]^{25}_{D} = -6.6°$ (*c* 1.18, 1,4-dioxane), while the polymer obtained after 24 h displayed a quite small value of $[\alpha]^{25}_{D} = -0.7°$ (*c* 1.14, 1,4-dioxane). The fact that racemization occurred at the later stages of the polymerization also proves the existence of the chain scission and the chain recombination reactions in the case of using *t*-BuOK as an initiator.

Conclusion

Optically pure (*S*)-2-(1-naphthyl)-2-phenyl-5,5-dimethyl-1-oxa-2,5-disilacyclopentane ((*S*)-**1**) was synthesized via intramolecular hydrosilylation in good yield. Anionic ROP of this cyclic compound was achieved successfully. When *t*-BuOK was used as an initiator, a significant degree of chain scission occurred, which resulted in the formation of the racemized low molecular weight cyclic polymer and cyclic dimers. On the other hand, polymerization using PhLi not only afforded a high yield of the linear polymer with a controlled molecular weight and a rather narrow molecular weight distribution but is also highly regioselective, conferring on the resulting polymer a high isotacticity and a high optical purity.

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References and Notes

(1) (a) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (b) West, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York, 1989; p 1207. (c) *Silicon-Containing Polymers*; Richard, G. J., Ed.; The Royal Society of Chemistry: Cambridge, 1995. (d) Birot, M.; Pillot, J.; Dunognes, J. *Chem. Rev.* **1995**, *95*, 1443.

(2) (a) Weyenberg, D. R.; Nelson, L. E. *J. Org. Chem.* **1965**, *30*, 2618. (b) Bamford, W. R.; Lovie, J. C.; Watt, J. A. C. *J. Chem. Soc. C* **1966**, 1137. (c) Nametkin, N. S.; Vdovin, V. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, 1153. (d) Matyjaszewski, K.; Chen, Y. L.; Kim, H. K. *ACS Symp. Ser.* **1988**, *360*, 78. (e) Cypryk, M.; Gupta, Y.; Matyjazewski, K. *J. Am. Chem. Soc.* **1991**, *113*, 1046. (f) Matyjazewski, K.; Cypryk, M.; Frey, H.; Hrkach, J.; Kim, H. K.; Moeller, M.; Ruehl, K.; White, M. *J. Macromol. Sci., Chem.* **1991**, *A28*, 1151.

(3) (a) Kriner, W. A. *J. Polym. Sci., Polym. Chem. Ed.* **1966**, *4*, 444. (b) Nametkin, N. S.; Vdvin, V. M.; Zav'yalov, V. I. *Dokl. Akad. Nauk SSSR, Ser. Khim.* **1965**, *162* (4), 824. (c) Nametkin, N. S.; Vdvin, V. M.; Zelenaya, A. V. *Dokl. Akad. Nauk SSSR, Ser. Khim.* **1965**, 162. (d) Wu, H. J.; Interrante, L. V. *Macromolecules* **1992**, *25*, 1840. (e) Suzuki, M.; Obayashi, T.; Kramer, W.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1994**, 553. (f) Suzuki, M.; Kotani, J.; Gyobu, S.; Kaneko, T.; Saegusa, T. *Macromolecules* **1994**, *27*, 2360. (g) Suzuki, M.; Obayashi, T.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1993**, 717. (h) Suzuki, M.; Kaneko, T.; Morishima, Y.; Obayashi, T.; Saegusa, T. *Polym. J.* **1996**, *28*, 16. (i) Interrante, L. V.; Liu, Q.; Rushkin, I.; Shen, Q. *J. Organomet. Chem.* **1996**, *521*, 1. (j) Shen, Q. H.; Interrante, L. V.; *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 3193. (k) Uhlig, W. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 725.

(4) (a) Armitage, D. A. In *Comprehensive Organometallic Chemistry*; Wlkinson, J., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, UK, 1982; Vol. 2, p 162. (b) Barton, T. J. In *Comprehensive Organometallic Chemistry*; Wlkinson, J., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, UK, 1982; Vol. 2, p 205.

(5) Corey, J. Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York, 1989; pp 8−18.

(6) (a) Hyde, J. F. U.S. Patent 2,490,357, 1949. (b) Morton, M.; Deisz, M. A.; Bostick, E. E. *J. Polym. Sci.* **1962**, *A2*, 513. (c) Shinohara, M. *Polym. Prepr.* **1973**, 1209. (d) Chojnowski, J.; Mazurek, M. *Makromol. Chem.* **1975**, *176*, 2999. (e) Molenberg, A.; Michalke, D.; Moller, M.; Pieper, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 169.

(7) Piccoli, W. A.; Haberland, G. G.; Merker, R. L. *J. Am. Chem. Soc.* **1960**, *82*, 1883.

(8) (a) Suryanarayana, B.; Peace, B. W.; Mayhan, K. G. *J. Polym. Sci.* **1974**, *12*, 1089. (b) Suryanarayana, B.; Peace, B. W.; Mayhan, K. G. *J. Polym. Sci.* **1974**, *12*, 1109.

(9) Samara, M.; Loy, D. A. *Polym. Prep.* **1998**, *39* (1), 556.

(10) Sommer, L. H.; Ansul, G. R. *J. Am. Chem. Soc.* **1955**, *77*, 2482.

(11) Li, Y.; Kawakami, Y. *Macromolecules* **1998**, *31*, 5592.

(12) Karstedt, B. D. U.S. Patent 3,775,452, 1973.

(13) Ito, K.; Hashizuka, Y.; Yamashita, Y. *Macromolecules* **1977**, *10*, 821.

(14) Compound **7** was prepared following the method reported by: Belmonte, P. A.; Own, Z. Y. *J. Am. Chem. Soc.* **1984**, *106*, 7493. Compound **9** was prepared by the procedure described in: *Organic Syntheses*; Noland, W. E., Ed.; John Wiley and Sons: New York, 1988; Vol. 6, p 354. Compounds **8** and **10** were prepared following the methods reported by: Sommer, L. H.; Frye, C. L.; Mosolf, M. C.; Parker, G. A.; Rodewald, P. G.; Michael, K. W.; Okaya, Y.; Pepinsky, R. *J. Am. Chem. Soc.* **1961**, *83*, 2210.

(15) (a) Benouargha, A.; Boutevin, B.; Caporiccio, G.; Essassi, E.; Guida-Pietrasanta, F.; Ratsimihety, A. *Eur. Polym. J.* **1997**, *33*, 1117. (b) Ameduri, B.; Boutevin, B.; Guida-Pietrasanta, F.; Manseri, A.; Ratsimihety, A.; Caporiccio, G. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 3077.

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